

Radial Behavior of Gradient Expansion Approximation to Atomic Fukui Function and Shell Structure of Atoms

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ABSTRACT: An approximation to the Fukui function in atoms recently proposed in the form of a gradient correction to the local density approximation expression is here investigated. The spatial behavior of this function is analyzed, focusing on the gradient correction term. Physical information on the shell structure of atoms is shown to be conveyed by the radial distribution of that term. The analytically modeled densities (AMD) procedure is also implemented, and global atomic hardnesses are calculated with Hartree-Fock and AMD representations of atomic electron densities. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 488–503, 1998

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Introduction

Formal developments and methodological advances in density functional theory (DFT) have recently provided rigorous support to qualitative concepts traditionally used in chemistry.^{1–8}

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Especially relevant for reactivity studies are concepts like chemical potential (electronegativity), chemical hardness, and the Fukui function. Much attention has been paid in recent years to these topics in DFT developments, and particular emphasis has been placed on the hardness and softness concepts. This interest has been motivated mainly by the search for rationalization and understanding of principles traditionally rooted in chemistry (hard and soft acids and bases behavior,^{1,2} for example) that are currently being considered from new perspectives provided by DFT. Particularly

important for reactivity is the maximum hardness principle (MHP) suggested by Pearson² who has pointed out that molecules tend to rearrange to achieve maximum hardness. Based on new functional expansion methods, Liu and Parr³ recently developed theoretical relationships between the total energy of atomic and molecular systems and the aforementioned chemical quantities and have also provided new insight into the understanding of the MHP.

A number of theoretical methods of interest in reactivity depend on the calculation of the Fukui function. Hardness itself can be expressed as a density functional involving this function. However, due to the considerable difficulties in obtaining this function *a priori*, all the attempts to compute it have relied on several approximations, the most widely used being those based on Fukui's frontier orbital theory.⁹ Chattaraj, Cedillo, and Parr (CCP)¹⁰ have recently proposed a new approximation to calculate the Fukui function that needs only

the electron density of the neutral species and incorporates a gradient correction term. Due to the potential importance of this approximation in reactivity studies, we here analyze the information obtainable from its spatial behavior in connection with the atomic shell structure and calculation of atomic hardnesses.

First, a brief presentation of the Fukui function is given. The CCP approach incorporating gradient corrections to the local density approximation (LDA) formula is then recalled. We then explore the spatial behavior of the CCP Fukui function, and its radial distribution; special attention is paid to the gradient correction term. We show that information closely related to the shell structure of atoms may be extracted from the gradient correction. The application of the analytically modeled densities (AMD) procedure developed by us^{11,12} to the calculation of the Fukui function is presented. We finally analyze atomic hardnesses computed with Hartree-Fock (HF) atomic densities and the AMD functions.

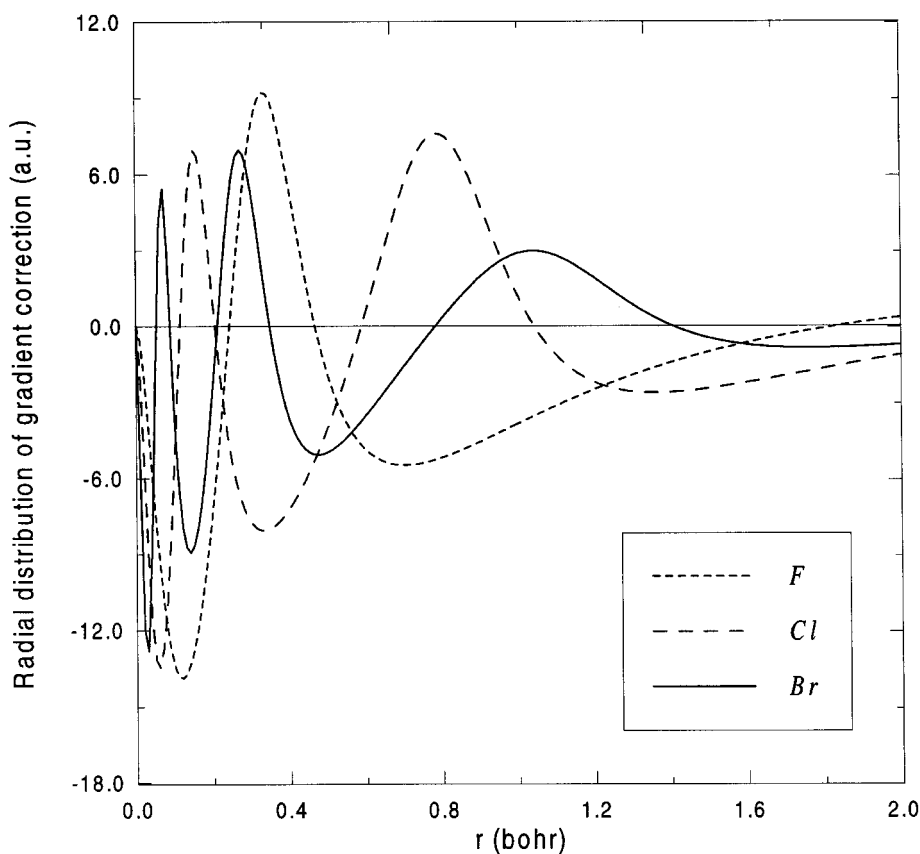


FIGURE 1. Radial distribution of the gradient correction φ/N term in eq. (12) for F, Cl, and Br atoms in the inner radial region (0.0, 2.0 bohr) computed with HF densities.

Fukui Function

For an N -electron system of density $\rho(\mathbf{r})$ and external potential $\nu(\mathbf{r})$, the energy change from one ground state to another is given by the differential expression¹

$$dE = \mu dN + \int \rho(\mathbf{r}) d\nu(\mathbf{r}) d\mathbf{r}, \quad (1)$$

if the energy is assumed to be a continuous and differentiable function of N and ν . The coefficient μ is the chemical potential, actually the negative of the electronegativity χ ,^{1,4}

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{\nu} = -\chi. \quad (2)$$

An expression analogous to (1) exists for changes in the chemical potential,

$$d\mu = 2\eta dN + \int f(\mathbf{r}) d\nu(\mathbf{r}) d\mathbf{r}, \quad (3)$$

where η is the global hardness of the system,^{1,5}

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{\nu} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{\nu}, \quad (4)$$

and $f(\mathbf{r})$ is a quantity called the Fukui function,^{1,6} defined as

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{\nu} = \left(\frac{\delta \mu}{\delta \nu(\mathbf{r})} \right)_N. \quad (5)$$

Equation (3) links three quantities of special chemical relevance to the number of electrons and the external potential. While μ and η are numbers representing global properties of the system, f is a local property that depends on \mathbf{r} . It has been shown^{7,8} that the global hardness can be determined from the integral

$$\eta = \frac{1}{N} \iint \eta(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') \rho(\mathbf{r}) d\mathbf{r}' d\mathbf{r}, \quad (6)$$

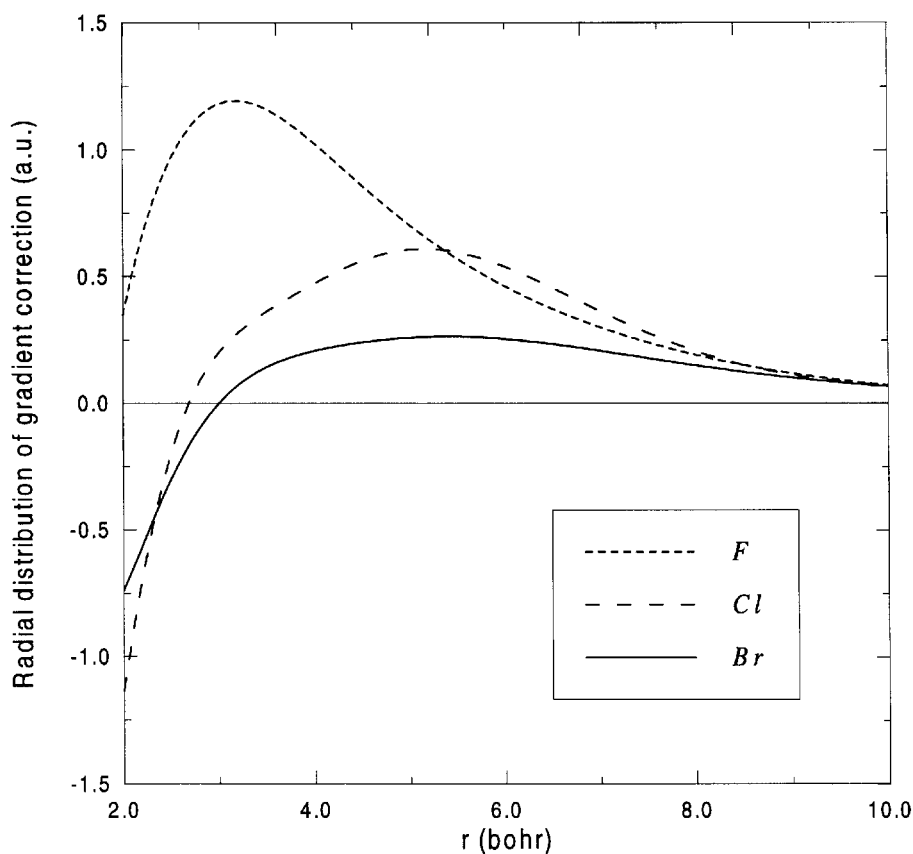


FIGURE 2. Radial distribution of the gradient correction φ/N term in eq. (12) for F, Cl, and Br atoms in the outer radial region (2.0, 10.0 bohr) computed with HF densities.

in which the Fukui function is also present and where the hardness kernel is given by⁸

$$\eta(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 F[\rho]}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \quad (7)$$

$F[\rho]$ being a universal functional for the sum of kinetic and electron–electron repulsion energies.¹ Because of the great difficulty in computing hardnesses with (6) and (7), simple approximations have been proposed in the past. Those based on finite difference methods allow the estimation of η from the first ionization potential I and the electron affinity A in the form of the $\eta = (I - A)/2$ expression parallel to the famous Mulliken formula $\chi = (I + A)/2$ for the electronegativity. By using Koopmans theorem, Pearson² has proposed obtaining hardness from the eigenvalues ε of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as $\eta = (\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})/2$.

The other quantity, the Fukui function, is a local (position-dependent) property of the system con-

ventionally considered as a reactivity parameter in the sense of Fukui's frontier orbital theory⁹ and measures the sensitivity of the chemical potential at \mathbf{r} to external perturbations. For integer N , the derivative of $\rho(\mathbf{r})$ in (5) is not continuous,¹³ but the derivative taken from the left, $N - \delta N$, may differ from the derivative taken from the right, $N + \delta N$, as $\delta N \rightarrow 0$. This discontinuity may be employed to measure reactivity properties of the system: while the left-hand derivative, $f^-(\mathbf{r})$, provides information on sites of electrophilic attack, the right-hand derivative, $f^+(\mathbf{r})$, measures reactivity toward nucleophilic reagents; the average of both informs about reactivity toward radical reagents.⁶ It has been also argued^{1,6} that the most reactive site is associated with the maximum response of the chemical potential, that is, the site having the largest $f(\mathbf{r})$ value.

It follows from DFT that the Fukui function is a universal functional of the density. However, because the functional form needed to obtain $f(\mathbf{r})$ from (5) is not known, a number of approxima-

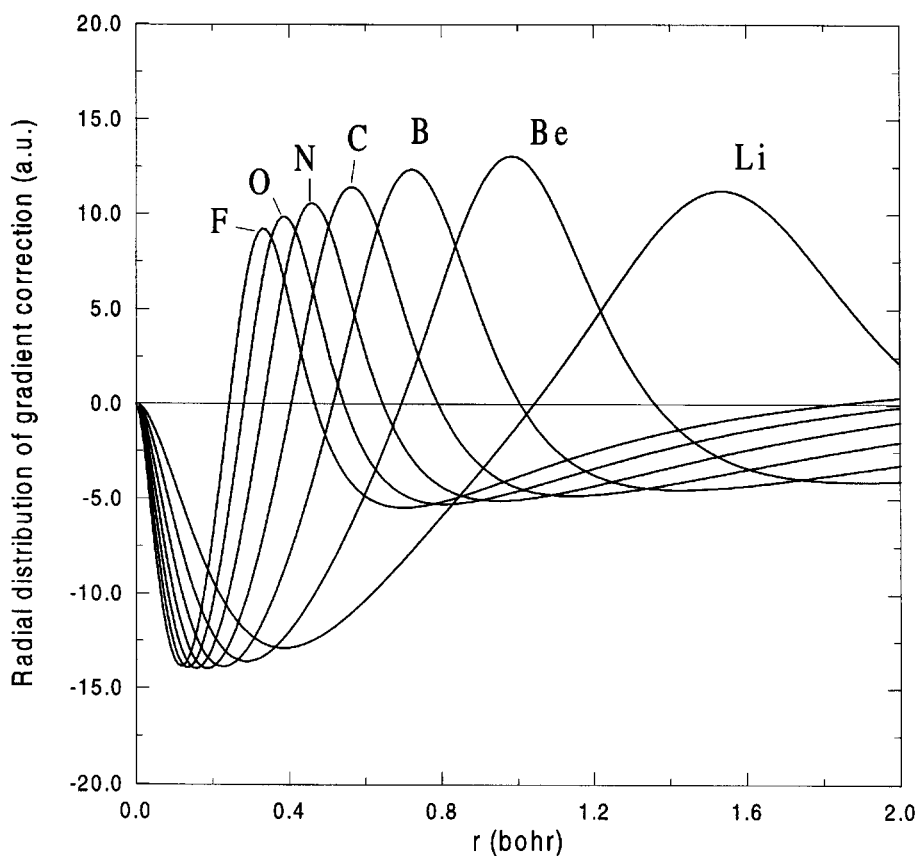


FIGURE 3. Radial distribution of the gradient correction φ/N term in eq. (12) for first-row Li-F atoms in the inner radial region (0,0, 2.0 bohr) computed with HF densities.

tions have been introduced in the past. The most widely used procedure, based on the original ideas by Fukui, has assumed that the HOMO and LUMO electron densities are estimates of $f^-(\mathbf{r})$ and $f^+(\mathbf{r})$, respectively. Although very useful as a practical tool in semiquantitative studies on reactivity, this is a severe simplification: in view of the importance of $f(\mathbf{r})$ it is evident that more satisfactory approaches are needed. Most of the models proposed in recent years¹⁴⁻¹⁶ require not only the calculation of the Fukui function on the neutral system but also on its negative and positive ions, which is a serious computational drawback. Although given the universal functional character of $f(\mathbf{r})$, it is possible *in principle* to compute the Fukui function from $\rho(\mathbf{r})$ only; developing such a procedure is a difficult problem. The first attempt in this regard has been presented by CCP¹⁰ who developed an approach to compute $f(\mathbf{r})$ by including a gradient correction to the LDA expression.

Formula for Fukui Function Including Gradient Correction

In a constant external potential ν , the Fukui function (5) for an N -electron homogeneous gas constrained to a volume V with density $\rho(\mathbf{r}) = N/V$ is

$$f(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{\nu} = \frac{1}{V} = \frac{\rho(\mathbf{r})}{N}. \quad (8)$$

If the system were homogeneous, both $f(\mathbf{r})$ and $\rho(\mathbf{r})$ should be constant, of course, but for the inhomogeneous case both terms are spatial functions and this expression represents the local density approximation to the Fukui function.

CCP then modify the LDA formula (8) by including inhomogeneity corrections through an ex-

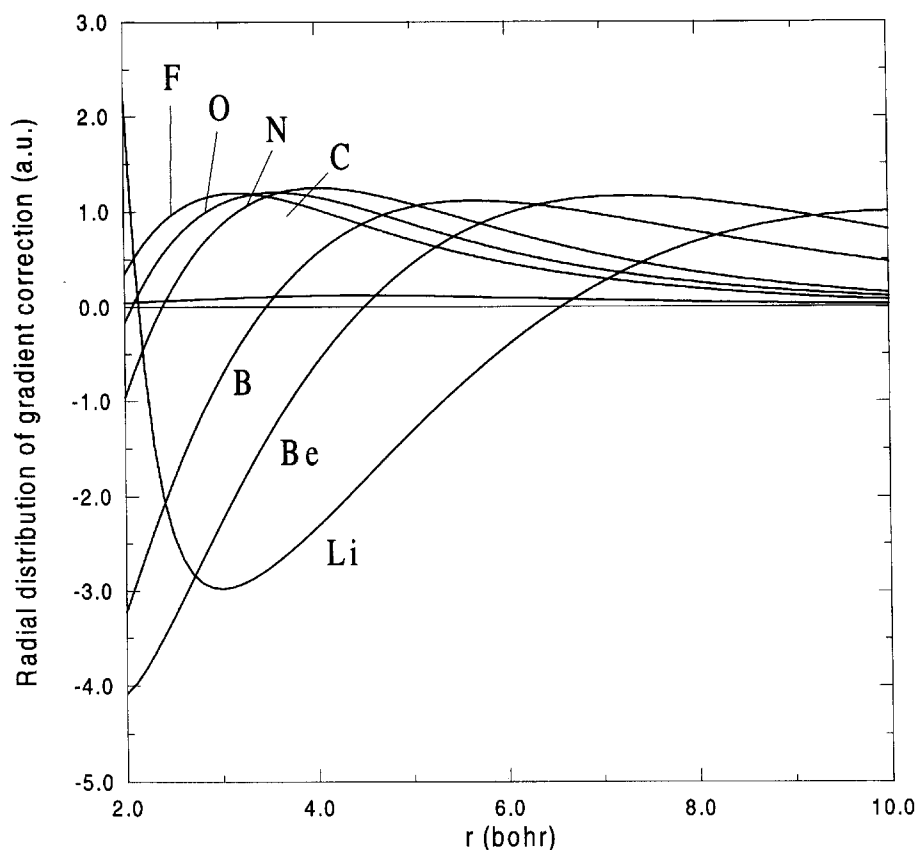


FIGURE 4. Radial distribution of the gradient correction φ/N term in eq. (12) for first-row Li-F atoms in the outer radial region (2.0, 10.0 bohr) computed with HF densities.

pansion of the type¹⁰

$$f(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N} [1 + \alpha \Phi(\mathbf{r}; \rho, \nabla \rho, \nabla^2 \rho, \dots)], \quad (9)$$

where α is the only parameter present. The correction must satisfy two requirements: Φ should be dimensionless and the Fukui function should be normalized, $\int f(\mathbf{r}) d\mathbf{r} = 1$ (there are no approximations up to this point). To fulfill both conditions, CCP consider the product $\rho\Phi$ as the divergence of some vector field and propose for the correction the form

$$\Phi \approx \frac{1}{\rho} \nabla \cdot \left(\frac{\nabla \rho}{\rho^{2/3}} \right), \quad (10)$$

involving only up to second-order derivatives in the expansion (9). To avoid the divergence of this Φ at the origin, the authors add another term to (10) that removes this undesired feature while still

satisfying the above conditions. The final result is

$$f(\mathbf{r}) = \frac{\rho(\mathbf{r})}{N} + \alpha \frac{\rho_0^{-2/3}}{N} \left\{ \left[\left(\frac{\rho_0}{\rho} \right)^{2/3} - 1 \right] \nabla^2 \rho - \frac{2}{3} \left(\frac{\rho_0}{\rho} \right)^{2/3} \frac{\nabla \rho \cdot \nabla \rho}{\rho} \right\}, \quad (11)$$

where ρ_0 is the electron density at the nucleus. For simplicity, we write this expression as

$$f(\mathbf{r}) = \frac{\rho}{N} + \alpha \frac{\varphi}{N}, \quad (12)$$

where it is implied in the notation that ρ and φ are spatial functions.

The behavior of (12) with the parameter α as well as the cusp condition for $f(\mathbf{r})$ was recently studied¹⁷ using HF atomic wave functions¹⁸ to compute ρ . Different methods to determine α from various radial moments $\langle r^n \rangle$ computed over $f(\mathbf{r})$ were proposed in ref. 10. Assuming that no change on ρ is expected to occur in the core region when

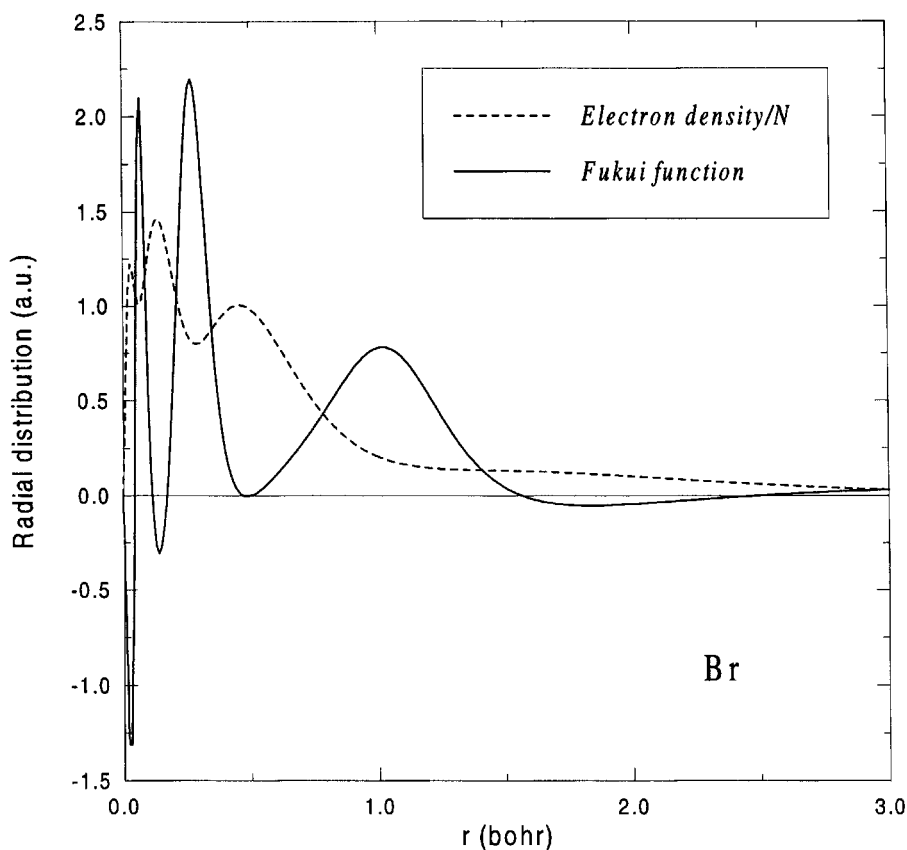


FIGURE 5. Radial distribution of the electron density ρ/N and Fukui function for the Br atom in the inner radial region (0.0, 3.0 bohr) computed with HF densities and $\alpha = 0.197$ in $f(\mathbf{r})$.

N changes in a chemical process, Pacios¹⁷ proposed a new set of α parameters. An alternative procedure to set α for an optimum fulfillment of the cusp condition was also suggested in both articles through different methods. In all cases, α values fell within the range (0.08, 0.20) for main-group atoms in the first three rows of the periodic table. Except for α based on the cusp condition, the different sets of α are close and lead to similar spatial behavior in spite of the large discrepancies found when computing hardnesses (see below). These issues are addressed below from new perspectives emphasizing the search for information not depending on α .

Radial Distribution of Gradient Correction

We determined radial distributions of the gradient correction term, $4\pi r^2\varphi/N$, with φ defined in (11) and (12), for the main-group elements in the

first three rows of the periodic table using HF atomic densities. Figure 1 shows $4\pi r^2\varphi/N$ for fluorine, chlorine, and bromine in the inner 0.0–2.0 bohr radial region; Figure 2 displays the outer atomic region up to 10 bohr. Because φ/N represents the inhomogeneity of the electron density, it is associated to changes of curvature in ρ through the operators in (11). This is the reason for the pronounced oscillatory behavior in the inner atomic region. Every radial distribution of φ/N exhibits n minima, n maxima, and $2n - 1$ radial distances r_0 at which $\varphi(r_0) = 0$ [points where the Fukui function reduces to $\rho(r_0)/N$], n being the principal quantum number. To compare $4\pi r^2\varphi/N$ within a row, we plot in Figure 3 curves for Li-F atoms in the inner 0.0–2.0 bohr radial region and in Figure 4 the outer 2.0–10.0 bohr region. Whereas the location of the innermost minimum lies approximately at the same radial distance for all atoms, the first maximum is shifted toward lower radial distances as Z increases, a feature also shown by the outer maximum in Figure 4. As for

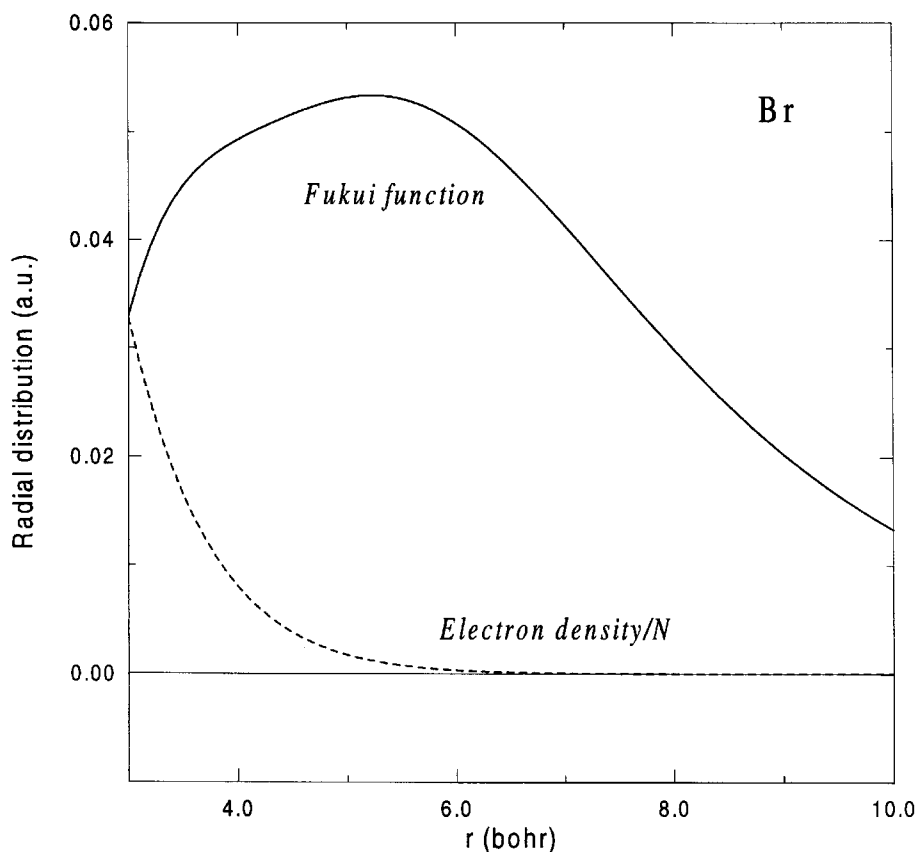


FIGURE 6. Radial distribution of the electron density ρ/N and Fukui function for Br atom in the outer radial region (3.0, 10.0 bohr) computed with HF densities and $\alpha = 0.197$ in $f(r)$.

these plots, the decay of $4\pi r^2\varphi/N$ (quantity not depending on α) is markedly slower for electropositive atoms in outer regions.

As discussed in ref. 17, different values of α lead to considerable deviations in hardnesses computed with eq. (6). However, with regard to the spatial behavior of $f(\mathbf{r})$, the variations are noticeable only near the nucleus. We plot in Figure 5 the radial distribution of the Fukui function, $4\pi r^2 f(\mathbf{r})$, for bromine computed with $\alpha = 0.197$, the value obtained from the criterion proposed by Pacios.¹⁷ The $4\pi r^2 p/N$ curve displaying the characteristic shape of the radial distribution of electron density is overimposed in this figure, that covers the 0.0–3.0 bohr region. Except for the scale, the radial distribution of $f(\mathbf{r})$ is similar to the gradient correction alone in Figure 1. Particularly interesting for reactivity purposes is the region outside the crossing point at $r_0 = 0.78$ bohr. The computed Fukui function exhibits inhomogeneities in a spatial region where $\rho(\mathbf{r})$ hardly displays any features other than the almost monotonical decrease. The outermost region starting at the outer crossing

point r_0 at 3.0 bohr is displayed in Figure 6. While $\rho(\mathbf{r})$ falls practically to zero at 5.0 bohr, the Fukui function has an outer maximum at 5.4 bohr and decreases rapidly afterward.

Shell Structure from Gradient Correction

Basic features in the radial behavior of the Fukui function have been shown to depend in large part on the gradient correction term. By exploring its relationship with the shell structure of atoms, this section tests whether this spatial behavior conveys some physical information. There has been interest for a long time in this issue as a challenging test for various functions and functionals of the spherically averaged electron density $\rho(\mathbf{r})$ in atoms.^{19–25} Recently, the shell structure has been related with the inflection points in the radial distribution of $\rho(\mathbf{r})$.²² Sen et al.^{23,24} have also recovered the shell structure from the maxima in the average local electrostatic potential (ALEP) $V(\mathbf{r})/\rho(\mathbf{r})$.

TABLE I.
Radial Location of n Maxima in Radial Distribution of Gradient Correction Term φ/N , r_i (bohr), and Electron Charges Integrated in Intervals $(0, r_1)$, q_1 , (r_1, r_2) , $q_2, \dots, (r_n, \infty)$, q_{out} , for Main-Group Elements Li Through Kr.

| Atom | r_1 | r_2 | r_3 | r_4 | q_1 | q_2 | q_3 | q_4 | q_{out} |
|------|--------|-------|-------|-------|-------|-------|--------|-------|------------------|
| Li | 1.54 | 10.3 | | | 2.001 | 0.997 | | | 0.002 |
| Be | 0.984 | 7.29 | | | 1.999 | 1.995 | | | 0.006 |
| B | 0.722 | 5.66 | | | 2.019 | 2.966 | | | 0.015 |
| C | 0.564 | 4.70 | | | 2.043 | 3.937 | | | 0.020 |
| N | 0.460 | 4.02 | | | 2.067 | 4.910 | | | 0.023 |
| O | 0.387 | 3.58 | | | 2.088 | 5.881 | | | 0.031 |
| F | 0.333 | 3.18 | | | 2.107 | 6.852 | | | 0.041 |
| Ne | 0.292 | 2.84 | | | 2.125 | 7.824 | | | 0.051 |
| Na | 0.258 | 2.09 | 11.1 | | 2.137 | 7.848 | 1.013 | | 0.002 |
| Mg | 0.232 | 1.58 | 8.74 | | 2.147 | 7.812 | 2.037 | | 0.004 |
| Al | 0.210 | 1.32 | 7.90 | | 2.155 | 7.799 | 3.035 | | 0.011 |
| Si | 0.192 | 1.13 | 6.78 | | 2.163 | 7.790 | 4.035 | | 0.012 |
| P | 0.177 | 0.989 | 6.04 | | 2.169 | 7.785 | 5.035 | | 0.011 |
| S | 0.163 | 0.880 | 5.51 | | 2.171 | 7.797 | 6.020 | | 0.012 |
| Cl | 0.154 | 0.787 | 5.15 | | 2.181 | 7.778 | 7.027 | | 0.014 |
| Ar | 0.143 | 0.714 | 4.56 | | 2.186 | 7.781 | 8.014 | | 0.019 |
| K | 0.134 | 0.652 | 3.01 | 13.0 | 2.191 | 7.775 | 8.013 | 1.019 | 0.002 |
| Ca | 0.126 | 0.599 | 2.38 | 9.90 | 2.195 | 7.769 | 7.969 | 2.057 | 0.010 |
| Ga | 0.0775 | 0.320 | 1.42 | 8.29 | 2.219 | 8.206 | 16.906 | 3.662 | 0.007 |
| Ge | 0.0749 | 0.306 | 1.31 | 7.12 | 2.221 | 8.239 | 16.971 | 4.560 | 0.009 |
| As | 0.0724 | 0.293 | 1.21 | 6.15 | 2.222 | 8.269 | 17.002 | 5.492 | 0.015 |
| Se | 0.0700 | 0.281 | 1.13 | 5.94 | 2.224 | 8.290 | 17.044 | 6.429 | 0.013 |
| Br | 0.0678 | 0.271 | 1.04 | 5.40 | 2.225 | 8.322 | 16.984 | 7.450 | 0.019 |
| Kr | 0.0658 | 0.261 | 0.972 | 4.72 | 2.227 | 8.343 | 16.968 | 8.426 | 0.036 |

We list in Table I the radial locations of the n maxima in the radial distribution of the gradient correction term φ/N analyzed in the last section. Electron charges integrated in $(0, r_1), (r_1, r_2), \dots, (r_n, \infty)$ are also given in this table for the main-group elements Li through Kr. The overall shell structure is clearly revealed. The location of the first maximum in $4\pi r^2\varphi/N$, r_1 , delimits the first K shell with integrated charges increasingly larger than 2.0 for heavier atoms. The second interval (r_1, r_2) encloses the L shell; integrated charges q_2 deviate from the aufbau principle as follows. For second-row elements, as well as potassium and calcium, part of this charge is shifted toward the inner K shell so that Na-Ca atoms have q_2 about 7.8. On the contrary, in atoms with the $3d$ orbital filled, this interval happens to enclose a slightly larger charge shifted from the outer (r_2, r_3) interval so that Ga-Kr atoms exhibit q_2 about 8.3. Finally, the M shell delimited by (r_2, r_3) , encloses in Ga-Kr elements encloses an integrated charge q_3

one unit lower than the expected value of 18. Besides the mentioned shift toward q_2 , part of the charge is now also placed at the outer interval (q_4 charge in Table I). These anomalies in the partition of electron charge between the M shell and $n = 4$ contributions may be linked to the smooth behavior of $\rho(r)$ in the radial atomic region where $3d, 4s$, and $4p$ electrons move. The electron density in this region does not allow an exact partition of electron charge, so one should not expect strict agreement with the aufbau principle at this boundary. The last column in Table I gives the residual charge integrated in (r_n, ∞) . Except for the O, F, Ne, and Kr atoms, it is below 0.03, a negligible contribution to the valence electron charge.

Politzer and Parr²⁵ proposed the location of the outermost minimum in the radial distribution of $\rho(r)$ as a physically meaningful boundary between core and valence regions in atoms. More recently, Sen et al.^{23,24} suggested the location of the outermost maximum in the ALEP function $V(r)/\rho(r)$ as

TABLE II. Core Radius r_c (bohr), Core Electron Charge q_c , and Valence Electron Charge q_v Computed from Location of Outermost Maximum in Average Local Electrostatic Potential $V(r)/\rho(r)$ and in Radial Distribution of Gradient Correction φ/N .

| Atom | $V(r)/\rho(r)^a$ | | | φ/N^b | | |
|------|------------------|--------|-------|---------------|--------|-------|
| | r_c | q_c | q_v | r_c | q_c | q_v |
| Li | 1.63 | 2.020 | 0.980 | 1.54 | 2.001 | 0.999 |
| Be | 1.03 | 2.020 | 1.980 | 0.984 | 1.999 | 2.001 |
| B | 0.751 | 2.048 | 2.952 | 0.722 | 2.019 | 2.981 |
| C | 0.579 | 2.065 | 3.935 | 0.564 | 2.043 | 3.957 |
| N | 0.473 | 2.093 | 4.907 | 0.460 | 2.067 | 4.933 |
| O | 0.394 | 2.108 | 5.892 | 0.387 | 2.088 | 5.912 |
| F | 0.336 | 2.118 | 6.882 | 0.333 | 2.107 | 6.893 |
| Ne | 0.289 | 2.112 | 7.888 | 0.292 | 2.125 | 7.875 |
| Na | 2.32 | 10.064 | 0.936 | 2.09 | 9.985 | 1.015 |
| Mg | 1.73 | 10.080 | 1.920 | 1.58 | 9.959 | 2.041 |
| Al | 1.42 | 10.081 | 2.919 | 1.32 | 9.954 | 3.046 |
| Si | 1.19 | 10.062 | 3.938 | 1.13 | 9.953 | 4.047 |
| P | 1.03 | 10.061 | 4.939 | 0.989 | 9.954 | 5.046 |
| S | 0.910 | 10.057 | 5.943 | 0.880 | 9.968 | 6.032 |
| Cl | 0.810 | 10.047 | 6.953 | 0.787 | 9.959 | 7.041 |
| Ar | 0.737 | 10.073 | 7.927 | 0.714 | 9.967 | 8.033 |
| K | 3.35 | 18.099 | 0.901 | 3.01 | 17.979 | 1.021 |
| Ca | 2.57 | 18.098 | 1.902 | 2.38 | 17.933 | 2.067 |
| Ga | 1.70 | 28.094 | 2.906 | 1.42 | 27.331 | 3.669 |
| Ge | 1.49 | 28.067 | 3.933 | 1.31 | 27.431 | 4.569 |
| As | 1.34 | 28.050 | 4.950 | 1.21 | 27.493 | 5.507 |
| Se | 1.22 | 28.022 | 5.978 | 1.13 | 27.558 | 6.442 |
| Br | 1.12 | 27.986 | 7.014 | 1.04 | 27.531 | 7.469 |
| Kr | 1.03 | 27.939 | 8.061 | 0.972 | 27.538 | 8.462 |

^a Values computed with numerical HF densities taken from ref. 23.

^b This work. Computed with analytical HF densities.¹⁸

a measure of the core radius. We present in Table II core radii, r_c , core charges integrated in $(0, r_c)$, q_c , and valence charges integrated in (r_c, ∞) , q_v , for main-group Li-Kr elements. The first set of data corresponds to the outermost maximum in $V(r)/\rho(r)$ determined with numerical HF densities obtained from average over configuration calculations. The second set of data gives the core-valence partition from the outermost maximum in $4\pi r^2\varphi/N$. Both sets of core radii show an excellent linear correlation with a correlation coefficient of 0.998. Regarding electron charges and with the only exception of Ga-Kr atoms, our results are in better agreement with ideal charges from the aufbau principle than ALEP data. As for data in this table, the outermost maximum in $4\pi r^2\varphi/N$ seems to provide the best criterion currently available to partition the space into core and valence regions. Earlier attempts to use the gradient of the density to recover the shell structure were not particularly successful.^{19,20} However, because the local curvature of the electron density must change between shells, a function particularly sensitive to varia-

tions in curvature like φ may better reveal such changes, which should explain the slightly better recovery of the shell structure from $4\pi r^2\varphi/N$.

Fukui Function Calculated with Analytically Modeled Densities

A simple analytical representation of HF atomic densities has been developed recently^{11,12,26} in the form of compact expansions of exponential terms;

$$\rho(r) = \sum_{i=1}^M A_i \exp(-B_i r), \quad (13)$$

with $M = 3$ for first-row atoms and $M = 4$ for second- and third-row main-group atoms (the exact density for H is the particular case $M = 1$ with $A_1 = 1/\pi$, $B_1 = 2$). The known behavior of the spherically averaged electron density, namely, the monotonic decay from the only maximum at the nucleus, is a sound basis for this mathematical expression. The AMD were devised

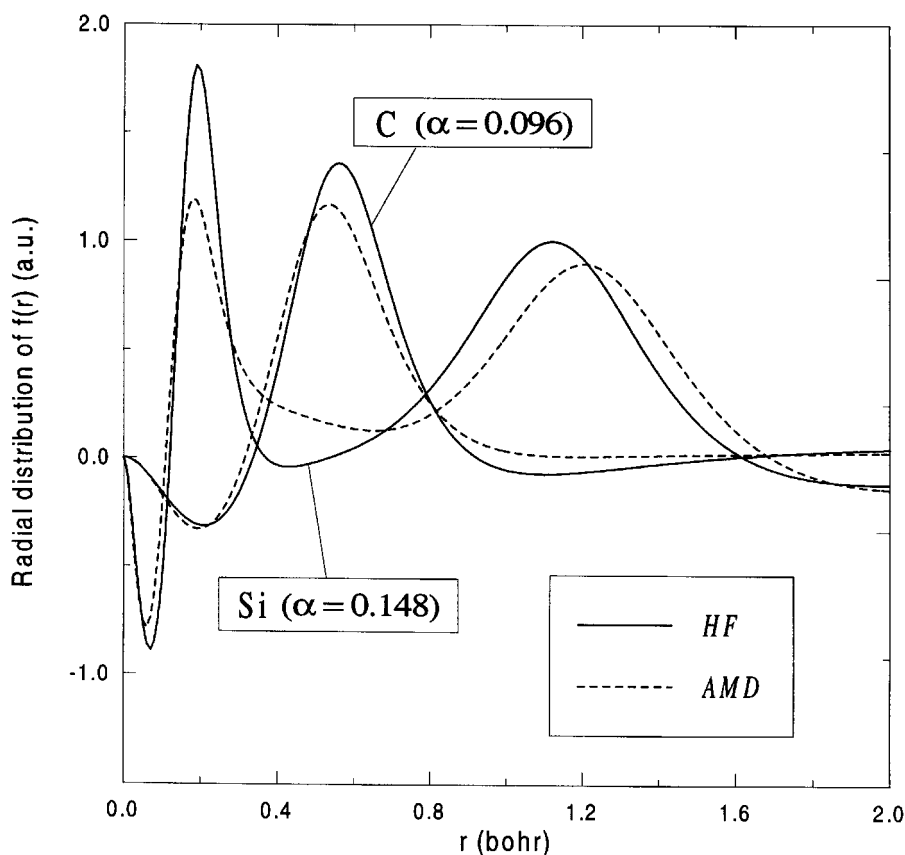


FIGURE 7. Radial distribution of the Fukui function for C and Si atoms in the inner radial region (0.0, 2.0 bohr) computed with HF densities and AMD functions.

as a step toward future basis set free DFT applications intended for large molecules. AMD also allow the development of simple analytical expressions for a wide range of functions and functionals while providing essentially the same physical information as HF densities.²⁶ Details of the procedure can be found in refs. 11 and 12. In brief, every atom is characterized by the set $\{A_i, B_i; i = 1, M\}$ fixed under conditions to reproduce HF-limit potential energy contributions, electron density at the nucleus, and radial expectation $\langle r^p \rangle$ values. The adequate representation of the long-range behavior of $\rho(\mathbf{r})$, as well as the normalization of the resulting AMD, are also imposed. Other properties not treated in the development of the model are also accurately determined: for instance, spatial behavior of $\rho(\mathbf{r})$ and associated functions,^{12,26} electrostatic potentials,^{11,12} correlation energies,¹² and kinetic functionals and spatial behavior of exchange potentials.²⁶

For possible further applications in reactivity, we consider the implementation of AMD into the

CCP definition of the Fukui function. Inserting (13) into (11) one gets

$$f(r) = \frac{1}{N} s_A(r) + \frac{\alpha}{N} \left[-\frac{2}{3} \frac{s_{AB}(r)^2}{s_A(r)^{5/3}} + \left\{ \frac{1}{s_A(r)^{2/3}} - \frac{1}{s_0^{2/3}} \right\} \times \left\{ s_{ABB}(r) - \frac{2}{r} s_{AB}(r) \right\} \right], \quad (14)$$

where

$$s_0 = \sum_{i=1}^M A_i, \quad (15a)$$

$$s_A(r) = \sum_{i=1}^M A_i \exp(-B_i r), \quad (15b)$$

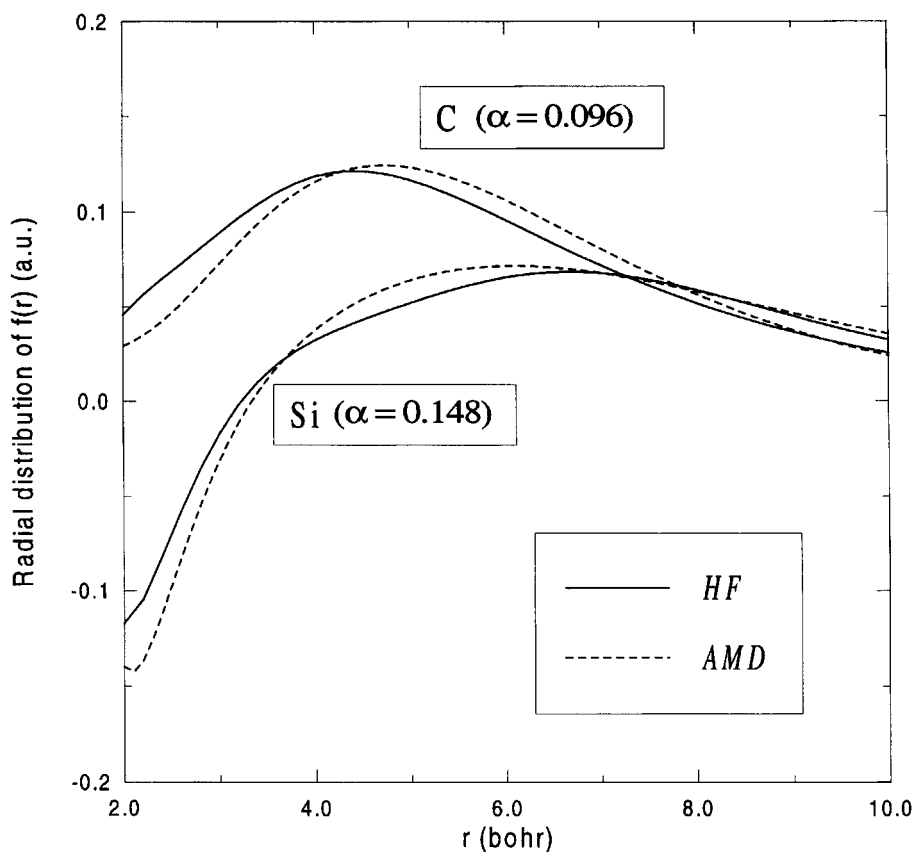


FIGURE 8. Radial distribution of the Fukui function for C and Si atoms in the outer radial region (2.0, 10.0 bohr) computed with HF densities and AMD functions.

$$s_{AB}(r) = \sum_{i=1}^M A_i B_i \exp(-B_i r), \quad (15c)$$

$$s_{ABB}(r) = \sum_{i=1}^M A_i B_i B_i \exp(-B_i r). \quad (15d)$$

Figures 7 and 8 display radial distributions of the Fukui function computed with HF densities and AMD for carbon and silicon. Because, strictly speaking, the densities involved in both distributions are different, α in (14) should be re-computed. However, we kept the parameters unchanged in this comparison to explore the performance of AMD when used instead of HF densities. Both distributions are in very good agreement for first-row elements in the whole radial space. On the contrary, second- and third-row atoms present small local discrepancies, especially at the inner minimum (about 0.5 bohr for Si in Fig. 7), although the location of the physically meaningful maxima is reasonably reproduced by AMD. Moreover, the region outside 2.0 bohr, which is especially interesting for reactivity, shows a particularly good agreement between HF and AMD distributions (note the scale in Fig. 8). The overall most noticeable difference is that because of the short expansions in (14), radial distributions of $\rho(\mathbf{r})$ and $f(\mathbf{r})$ are both smoother than the HF case, which is especially apparent in the large oscillations in the innermost core region (see also the related discussion in refs. 12 and 26).

Calculation of Atomic Hardnesses

The calculation of atomic global hardnesses η is a challenging application for any approximation to the Fukui function. Following a customarily used approximation, the universal functional $F[\rho]$ in the hardness kernel (7) can be written as

$$F[\rho] = T_0[\rho] + T_2[\rho] + J[\rho] + K_0[\rho] + E_C[\rho], \quad (16)$$

where $T_0[\rho]$ is the Thomas–Fermi (TF) kinetic functional, $T_2[\rho]$ a gradient correction to the TF functional, $J[\rho]$ the classical Coulomb repulsion energy, $K_0[\rho]$ the Dirac exchange functional, and $E_C[\rho]$ a correlation functional. (Any corrections to the exchange term are omitted in this approximation.) CCP computed η using one particular choice of the parameter in $f(\mathbf{r})$ (denoted α_1 in ref. 10). However, as previously demonstrated¹⁷ and here tested from a new point of view, very small changes in α lead to large variations in η . We

consider now the contributions to η arising from the terms in (16), irrespective of any particular parameter α . At this point, our aim is twofold: to separately evaluate the distinct contributions to η in order to establish the orders of magnitude implied and to gain insight into the reliability of the approximations used for computing hardnesses.

The global hardness can be written as a sum of terms arising from (16) as

$$\eta = \eta(T_0) + \eta(T_2) + \eta(J) + \eta(K_0) + \eta(E_C). \quad (17)$$

Using the known expressions for the terms in (16), determining the functional derivatives in (7), and writing $f(\mathbf{r})$ in the form of (12), each contribution to η in (17) can be split into two parts, one depending only on ρ/N and the other representing the gradient correction φ/N . The TF kinetic functional $T_0[\rho] = C_K \int \rho^{5/3} d\mathbf{r}$ leads to

$$\eta(T_0) = \frac{10}{9N^2} C_K \left[\int \rho^{5/3} d\mathbf{r} + \alpha \int \varphi \rho^{2/3} d\mathbf{r} \right], \quad (18)$$

where

$$C_K = \frac{3}{10} (3\pi^2)^{2/3} = 2.871234.$$

TABLE III.
Terms in Integrated Expression (24) of Atomic Global Hardness for HF Densities and AMD Functions (eV).

| Atom | HF | | AMD | |
|------|----------|----------|----------|----------|
| | <i>D</i> | <i>G</i> | <i>D</i> | <i>G</i> |
| H | 20.04 | −342.2 | 20.04 | −342.2 |
| Li | 40.08 | −412.7 | 39.76 | −413.6 |
| Be | 42.20 | −402.3 | 42.07 | −401.4 |
| B | 44.87 | −396.4 | 44.77 | −395.3 |
| C | 48.30 | −394.3 | 48.23 | −393.2 |
| N | 52.20 | −394.3 | 52.13 | −393.0 |
| O | 56.07 | −394.7 | 55.99 | −392.9 |
| F | 60.28 | −396.3 | 60.20 | −393.8 |
| Na | 66.36 | −396.1 | 66.26 | −388.7 |
| Mg | 68.03 | −394.5 | 67.95 | −386.6 |
| Al | 69.49 | −393.0 | 69.42 | −384.8 |
| Si | 71.06 | −391.9 | 71.01 | −381.1 |
| P | 72.71 | −391.1 | 72.68 | −379.4 |
| S | 74.35 | −390.3 | 74.37 | −377.8 |
| Cl | 76.04 | −390.0 | 76.09 | −376.9 |
| K | 78.69 | −388.7 | 78.60 | −384.2 |
| Ca | 79.59 | −387.7 | 79.51 | −383.2 |
| Ga | 97.25 | −386.5 | 97.39 | −385.8 |
| Ge | 98.41 | −386.3 | 98.63 | −387.0 |
| As | 99.56 | −386.1 | 99.86 | −389.4 |
| Se | 100.7 | −385.8 | 101.0 | −389.0 |
| Br | 101.8 | −385.7 | 102.0 | −388.2 |

The gradient correction $T_2[\rho]$ is one-ninth of the von Weizsäcker functional

$$T_W = \frac{1}{8} \int \frac{\nabla \rho \cdot \nabla \rho}{\rho} d\mathbf{r}$$

and gives rise to

$$\eta(T_2) = \frac{1}{36N^2} \left[\int - \frac{\nabla \rho \cdot \nabla \rho}{\rho} d\mathbf{r} + \alpha \int \varphi \left(\frac{\nabla^2 \rho}{\rho} - \frac{\nabla \rho \cdot \nabla \rho}{\rho^2} \right) d\mathbf{r} \right]. \quad (19)$$

$J[\rho]$ is the classical Coulomb repulsion term leading to the contribution

$$\eta(J) = \frac{1}{2N^2} \left[\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \iint \frac{\rho(\mathbf{r})\varphi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \right]. \quad (20)$$

$K_0[\rho]$ is the LDA Dirac exchange functional

$$K_0[\rho] = -C_X \int \rho^{4/3} d\mathbf{r}.$$

Its contribution to the total hardness is

$$\eta(K_0) = -\frac{4}{9N^2} C_X \left[\int \rho^{4/3} d\mathbf{r} + \alpha \int \varphi \rho^{1/3} d\mathbf{r} \right], \quad (21)$$

where

$$C_X = \frac{3}{4\pi} (3\pi^2)^{1/3} = 0.738559.$$

Finally, as a simple approximation to the (local) correlation functional, CCP considered the Wigner form

$$E_C = - \int \frac{\rho}{a + b\rho^{-1/3}} d\mathbf{r}, \quad (22)$$

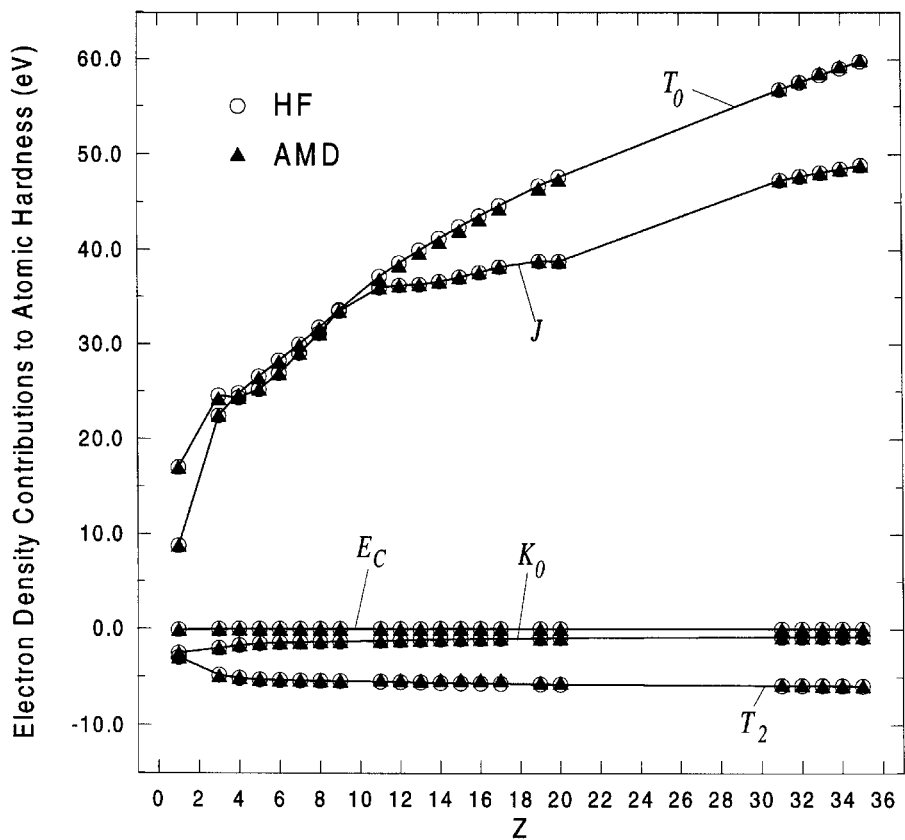


FIGURE 9. Contributions to global atomic hardness in eq. (17) arising from the ρ/N term in $f(\mathbf{r})$ for H-Br main-group elements excluding noble atoms. T_0 corresponds to the TF kinetic functional, T_2 is the gradient correction to T_0 , J is the classical Coulomb repulsion, K_0 is the Dirac exchange functional, and E_C is a Wigner-like local correlation functional given in eq. (22).

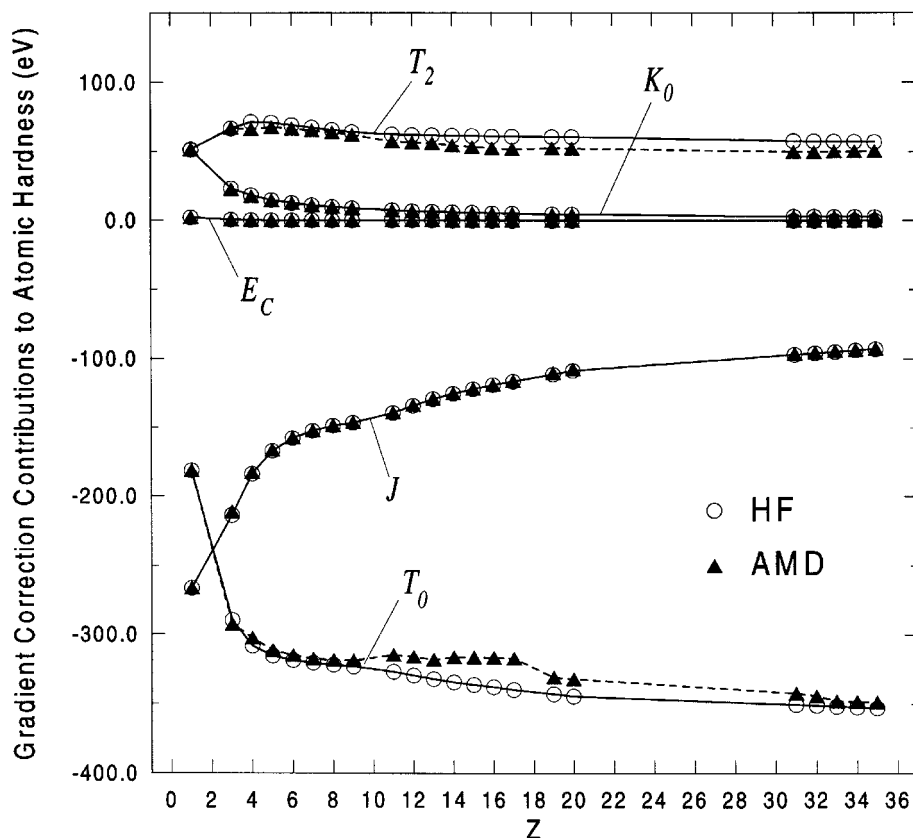


FIGURE 10. Contributions to global atomic hardness in eq. (17) arising from the φ/N term in $f(\mathbf{r})$ for H-Br main-group elements excluding noble atoms. T_0 corresponds to the TF kinetic functional, T_2 is the gradient correction to T_0 , J is the classical Coulomb repulsion, K_0 is the Dirac exchange functional, and E_C is a Wigner-like local correlation functional given in eq. (22).

with $a = 9.81$, $b = 21.437$. The corresponding contribution to the global hardness is

$$\eta(E_C) = -\frac{2\beta}{9N^2} \left[\int \rho^{4/3} \frac{2 + \gamma\rho^{1/3}}{(1 + \gamma\rho^{1/3})^3} d\mathbf{r} + \alpha \int \varphi\rho^{1/3} \frac{2 + \gamma\rho^{1/3}}{(1 + \gamma\rho^{1/3})^3} d\mathbf{r} \right], \quad (23)$$

where $\beta = 1/b = 0.046648$, $\gamma = a/b = 0.45762$.

After adding expressions (18)–(21) plus (23) and grouping factors due to the ρ/N and φ/N terms in the Fukui function, the global atomic hardness can be written as

$$\eta = D + \alpha G. \quad (24)$$

The values of D and G are listed in Table III for H-Br main group atoms, excluding noble atoms using both representations of $\rho(\mathbf{r})$, HF densities, and AMD. The five contributions due to ρ/N and φ/N terms are separately plotted in Figures 9 and

10, respectively. Except for small differences in kinetic T_0 and T_2 factors, HF and AMD results are almost indistinguishable. The numerical values of η are dominated by T_0 and J contributions, both positive in D and negative in G . T_2 and K_0 , both with the opposite sign to T_0 and J , account together for approximately 10% of D and 15% of G and are almost constant quantities from $Z \sim 4$ upward. The correlation contribution is essentially negligible. Note that, because this analysis is done with independence of any particular α in $f(\mathbf{r})$, it provides information about the CCP approximation itself insofar as the universal functional $F[\rho]$ in the hardness kernel is assumed to take the form of (16). In spite of the simplicity of the AMD, the basic features of the whole procedure remain unaltered with respect to HF densities.

As demonstrated before,¹⁷ the crucial point in computing acceptable η with the CCP approach happens to lie in the choice of the parameter α . Although the spatial behavior of $f(\mathbf{r})$ is to a great

extent independent of that choice, computed hardnesses are extremely sensitive to small changes in the parameter. This point is illustrated in Table IV, where HF and AMD η results obtained with (24) and D, G listed in Table III are presented for two sets of α . The first set, denoted α_0 , corresponds to the parameter that best fulfills the cusp condition on $f(\mathbf{r})$.^{10,17} The second set is calculated with the parameters obtained from the core criterion by Pacios¹⁷ (denoted α_C in Table IV). This set has been shown to exhibit the same features as the α_1 set of CCP in the absence of the T_2 contribution to η .¹⁷ Moreover, the numerical range of the distinct values proposed initially by these authors is very similar to the interval covered by α_0 and α_C in Table IV.

Due to the numerous approximations involved in the calculation of η , very close agreement with experimental values determined from $\eta = (I - A)/2$ ²⁷ must not be expected. However, inspecting Table IV we see that the α parameters fixed by criteria based on the spatial behavior of $f(\mathbf{r})$ are not consistent with reliable estimates of atomic hardnesses. For both α sets, calculated values of η are too large, especially in the α_0 case where they

increase with Z up to the point of yielding a wrong order of magnitude. Results for α_C are slightly better but, except for first-row atoms, errors on the order of 100% are present. On the other hand, α values simply taken to reproduce experimental data generally are not very far from the other existing α , a fact that demonstrates the extreme sensitivity of η to the parameter α . Data in Table IV show that AMD calculations perform much the same as HF calculations. For our purposes, it must be emphasized that the CCP representation of the Fukui function is in principle able to allow the calculation of atomic hardnesses through customary approximations to the universal functional $F[\rho]$. However, because the final calculation is so dependent on α , the best procedure to find this parameter remains to be found.

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TABLE IV.
Atomic Hardnesses η Computed with Eq. (24) and D, G Values in Table III for HF Densities and AMD Functions for Two Sets of Parameters α in $f(\mathbf{r})$ (α_0 and α_C), Experimental Hardnesses η_{exp} and α Value Reproducing η_{exp} for HF Densities, α_{exp} (η in eV).

| Atom | α_0 | $\eta^{\text{HF}}(\alpha_0)$ | $\eta^{\text{AMD}}(\alpha_0)$ | α_C | $\eta^{\text{HF}}(\alpha_C)$ | $\eta^{\text{AMD}}(\alpha_C)$ | η_{exp}^a | α_{exp} |
|------|------------|------------------------------|-------------------------------|------------|------------------------------|-------------------------------|-----------------------|-----------------------|
| Li | 0.0791 | 7.43 | 7.04 | 0.0773 | 8.18 | 7.79 | 4.78 | 0.0855 |
| Be | 0.0835 | 8.61 | 8.55 | 0.0867 | 7.32 | 7.27 | 9.00 | 0.0825 |
| B | 0.0859 | 10.82 | 10.81 | 0.0901 | 9.16 | 9.15 | 8.02 | 0.0930 |
| C | 0.0874 | 13.84 | 13.86 | 0.0932 | 11.55 | 11.58 | 10.00 | 0.0971 |
| N | 0.0885 | 17.30 | 17.34 | 0.0974 | 13.79 | 13.84 | 14.46 | 0.0957 |
| O | 0.0892 | 20.86 | 20.94 | 0.1121 | 11.82 | 11.95 | 12.16 | 0.1112 |
| F | 0.0899 | 24.66 | 24.79 | 0.1262 | 10.27 | 10.50 | 14.02 | 0.1167 |
| Na | 0.0913 | 30.20 | 30.77 | 0.1425 | 9.92 | 10.87 | 4.60 | 0.1559 |
| Mg | 0.0920 | 31.74 | 32.38 | 0.1425 | 11.82 | 12.86 | 7.80 | 0.1527 |
| Al | 0.0925 | 33.14 | 33.82 | 0.1424 | 13.53 | 14.62 | 5.54 | 0.1627 |
| Si | 0.0930 | 34.61 | 35.57 | 0.1422 | 15.33 | 16.82 | 6.76 | 0.1641 |
| P | 0.0934 | 36.19 | 37.25 | 0.1417 | 17.30 | 18.92 | 9.76 | 0.1610 |
| S | 0.0938 | 37.74 | 38.93 | 0.1421 | 18.89 | 20.69 | 8.28 | 0.1693 |
| Cl | 0.0943 | 39.26 | 40.55 | 0.1403 | 21.32 | 23.21 | 9.36 | 0.1710 |
| K | 0.0948 | 41.84 | 42.18 | 0.1577 | 17.39 | 18.01 | 3.84 | 0.1926 |
| Ca | 0.0951 | 42.71 | 43.07 | 0.1561 | 19.06 | 19.70 | 8.00 | 0.1846 |
| Ga | 0.0972 | 59.68 | 59.89 | 0.1964 | 21.34 | 21.62 | 5.80 | 0.2366 |
| Ge | 0.0973 | 60.83 | 60.97 | 0.1978 | 22.00 | 22.07 | 6.80 | 0.2372 |
| As | 0.0974 | 61.96 | 61.93 | 0.1981 | 23.08 | 22.72 | 9.00 | 0.2346 |
| Se | 0.0975 | 63.05 | 63.02 | 0.1988 | 23.96 | 23.62 | 7.74 | 0.2408 |
| Br | 0.0976 | 64.13 | 64.12 | 0.1971 | 25.76 | 25.49 | 8.44 | 0.2420 |

^a Reference 27. A factor of 2 is included according to definition (4).

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